

**PATENT**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Docket Number: DN 99-100

Application of: Michael B. Freeman et al.

Serial No: 09/727,324 : Group Art Unit: 1714

Filed: November 30, 2000 : Examiner: C. Shosho  
(Priority to 14-Dec-99)

Title: POLYMERIC BINDER FOR WATER-RESISTANT INKJET INKS

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Commissioner for Patents  
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Alexandria, VA 22313-1450

**SECOND DECLARATION UNDER 37 C.F.R. § 1.132**

I, Michael Paul Hallden-Abberton, declare and say that:

I. I am a citizen of the United States of America, residing at 964 Whitney Lane, Maple Glen, Pennsylvania. I graduated in 1973 from the State University of New York at Potsdam located in Potsdam, NY, with a BA. Degree in Chemistry. I graduated in 1978 from Ohio State University, located in Columbus, Ohio, with a Ph.D. Degree in Organic Chemistry. Since 1978 I have been working in the field of polymer chemistry at the Rohm and Haas Company. Since 1999 I have been a Research Fellow (senior research chemist) in the Exploratory Polymer Research and Architectural and Functional Coatings Departments of Rohm and Haas Company. I have been granted 19 patents in the field of polymer chemistry and I am the author of 17 papers in the polymer chemistry and organic chemistry fields. I am familiar with the above-identified

**CERTIFICATE OF TRANSMISSION**

I certify that this paper, along with any referred to as being attached or enclosed, is being facsimile transmitted to (703) 872-9311 under 37 CFR § 1.8 on the date indicated below and is addressed to Commissioner for Patents, PO Box 1450, Alexandria, VA 22313-1450.

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KARL STAUSS  
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patent application Serial No. 09/727,324 and with the European patent application published as EP 590604, cited by the Examiner in an office action dated February 7, 2003.

2. Under my direction, a number of samples of polymeric binders were prepared on behalf of Rohm and Haas Company and supplied to Lexmark International, Inc. for preparation of inks comprising said binders and for testing of printing properties. The tests compared (a) the effectiveness of the binder samples to adhere pigment to paper substrates as applied in an ink jet ink formulation by an ink jet printer as tested by wet rub, highlighter rub and smear resistance, and (b) the ability to print without clogging the printer head nozzles (referred to hereafter as printer head reliability). The polymer emulsions were prepared according to the technique described in the above-identified patent application.

3. In order to show criticality of the claimed particle size and glass transition temperature, the examples below were prepared and tested. Example 6 was previously made and reported in the July 1, 2003 declaration. This sample was retained as a control sample and a new ink was made with this binder as a control sample to show that results in this experiment were substantially similar to that previously run and reported. This control sample was also made because new printing equipment was needed to test the resulting inks on, and this example serves to show that the results are substantially similar to the old printing equipment. The following examples were prepared at sixty percent (60%) of the scale of the original patent application examples, all proportions being held to the original proportions on a per kilogram (/kg) of product basis. All Example numbers keep the same nomenclature as the previously submitted July 1, 2003 declaration.

4. Fluctuations in Tg and average particle size ranges are expected to one skilled in the art. Preparation of polymeric binder samples require use of varying amounts and types of monomers, leading to normal variations in Tg and average particle sizes. Tg variations of +/- 2°C are expected to one skilled in the art. Average particle size variations of +/- 15 nm are expected to one skilled in the art.

#### Example 6 – Repeat Sample from the July 1, 2003 Declaration and Re-Tested

In accordance with the invention a sample of butyl acrylate (BA), methyl methacrylate (MMA), and methacrylic acid (MAA) polymer was prepared according to the procedure in Example 4 of the present patent application (as a repeat control example) except that the sample was prepared at a smaller size (60% of Example 4), using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 628.5 g MMA, 649.8 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 1.8 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 10.5 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). After the co-feed was completed, the reaction was held at 81°C for 30 minutes. Then the product was cooled, filtered and neutralized with the neutralization accomplished by combining 1200 g of un-neutralized product with 1003 g deionized water and brought to a pH of 8.5 with KOH. The resultant polymer had an average particle size of 297 nm with a particle size distribution ranging from 190 nm to 435 nm. The calculated Tg was +20°C (actual Tg was +19°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 12 nozzles in the ink cartridge had misfired (196 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was intermediate (not as good as Example 1 from the July 1, 2003 Declaration, but better than an ink made without a binder).

#### Example 8

To show the effect of decreasing particle size (within the invention), at substantially the same Tg as Example 6, the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 628.5 g MMA, 649.8 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 2.4 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 9.9 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example #6. The resultant polymer had an average particle size of 272 nm with a particle size distribution ranging from 158 nm to 401 nm. The calculated Tg was +20°C (actual Tg was +18°C). In an assessment of printability, a sample ink containing 3.0% by weight of the

polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 45 nozzles in the ink cartridge had misfired (163 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was intermediate (not as good as Example 1 ( $T_g = -8^\circ\text{C}$ ), about the same as Example 6 ( $T_g = +19^\circ\text{C}$ ), and better than an ink made without a binder).

#### Example 9

To show the effect of decreasing particle size (outside the invention) at substantially the same  $T_g$  as Example 6, the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 628.5 g MMA, 649.8 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 3.9 g SLS (28.0%) was heated to  $81^\circ\text{C}$ . Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at  $81^\circ\text{C}$  for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 8.4 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example #6. The resultant polymer had an average particle size of 211 nm with a particle size distribution ranging from 109 nm to 317 nm. The calculated  $T_g$  was  $+20^\circ\text{C}$  (actual  $T_g$  was  $+18^\circ\text{C}$ ). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 103 nozzles in the ink cartridge had misfired (105 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was intermediate (not as good as Example 1 ( $T_g = -8^\circ\text{C}$ ), about the same as Example 6 ( $T_g = +19^\circ\text{C}$ ), and better than an ink made without a binder).

#### Example 10

To show the effect of decreasing particle size (outside the invention) at substantially the same  $T_g$  as Example 6, the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 628.5 g MMA, 649.8 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 4.6 g SLS (28.0%) was heated to  $81^\circ\text{C}$ . Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at  $81^\circ\text{C}$  for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 7.7 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example #6. The resultant polymer had an average particle size of 190 nm with

a particle size distribution ranging from 95 nm to 289 nm. The calculated Tg was +20°C (actual Tg was +17°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 156 nozzles in the ink cartridge had misfired (52 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was intermediate (not as good as Example 1 (Tg = -8C), about the same as Example 6 (Tg = +19C), and better than an ink made without a binder).

#### Example 11

To show the effect of decreasing particle size (outside the invention) at substantially the same Tg as Example 6, the procedure described in the preceding paragraph was repeated using a monomer mixture which consisted of 390g deionized water, 16.9 g MAA, 628.5 g MMA, 649.8 g BA and 6.3 g SLS (at 28% solids). In this case, a reaction vessel containing 680 g deionized, buffered water (0.122 meq buffer/g water) and 6.0 g SLS (28.0%) was heated to 81°C. Then 69.0 g of the monomer mix with a 12 g water rinse was added to the vessel followed by 3.36 g NaPS dissolved in 30 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 6.3 g SLS and a co-feed of 1.3 g NaPS in 60 g of water (added over 185 minutes). The sample was completed and neutralized as in Example #6. The resultant polymer had an average particle size of 172 nm with a particle size distribution ranging from 80 nm to 262 nm. The calculated Tg was +20°C (actual Tg was +16°C). In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated four times, an average of 189 nozzles in the ink cartridge had misfired (19 nozzles continued to fire). Performance in terms of wet-rub smear or resistance to smearing by highlighter pens was intermediate (not as good as Example 1 (Tg = -8C), about the same as Example 6 (Tg = +19C), and better than an ink made without a binder).

Once the print quality is determined to be poor, highlighter resistance is not applicable. The above Examples and test results, as well as the Examples and test results of the July 1, 2003 declaration, are summarized in the table below.

Sample	Avg. Particle Size (nm)	Min. to Max. Particle Size (nm)	Tg (°C)	Highlighter Resistance	Print Quality (Nozzle Test)
<b>Particle Size Variations with Tg around -9</b>					
Example 1	287	184-414	-8	Excellent	178/208 firing
Example 2	255	154-375	-9	Excellent	140/208 firing
Example 3	206	121-302	-8	N/A	52/208 firing
Example 4	182	88-273	-10	N/A	27/208 firing
Example 5	158	77-231	-10	N/A	1/208 firing
<b>Particle Size Variations with Tg around 18</b>					
Example 6 (Retested)	297	190-435	19	Intermediate	196/208 firing
Example 8	272	158-401	18	Intermediate	163/208
Example 9	211	109-317	18	N/A	105/208
Example 10	190	95-289	17	N/A	52/208
Example 11	172	80-262	16	N/A	19/208
<b>Tg Variations with Avg. Particle Size around 300</b>					
Example 1	287	184-414	-8	Excellent	178/208 firing
Example 6	297	190-435	19	Intermediate	156/208 firing
Example 7	311	198-456	33	Worst	178/208 firing

5. The above tests demonstrate criticality of particle size and Tg in the printer operability as measured by the number of nozzles that remain able to fire at the end of the printer test and the highlighter resistance property as measured by the relative optical appearance of the treated prints after rubbing with a highlighter as claimed in the above-identified patent application. In my opinion, the aforementioned criticality and superiority with respect to printer operability and highlighter resistance of the claimed invention is unobvious to one skilled in the art.

6. The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patents issuing thereon.

Respectfully submitted,

*Michael Hallden-Abberton*

Michael Hallden-Abberton

11 / 13 / 03

Date